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## MASS TRANSFER ACCOMPANIED BY REVERSIBLE CHEMICAL REACTIONS IN AN INERT POROUS SPHERE IMPREGNATED WITH A STAGNANT LIQUID

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**Abstract**—The absorption of gaseous components in porous particles impregnated with a reactive liquid phase has been studied theoretically. A model that describes this absorption process has been developed in which it is assumed that the porous particles act as a liquid support and are chemically inert. The model is based on the description of diffusion and reaction in a stagnant liquid sphere, and validated with several asymptotic analytical solutions. Both reactions instantaneous with respect to the mass transfer rate and reactions with finite reaction rates can be applied. For the instantaneous reactions an approximation for the dimensionless total accumulation is presented if the diffusivities of the absorbed gas and the other components are unequal. For reactions with finite rates different absorption regimes can be recognized in the time-flux diagrams. The simultaneous absorption of two gases which both react in the liquid-impregnated particles, e.g.  $\text{H}_2\text{S}$  and  $\text{CO}_2$  in aqueous amine solutions, has also been studied. The results of the simulations of the simultaneous absorption of two gases indicate that selective removal of one of the gas components with porous particles impregnated with a reactive liquid seems feasible.

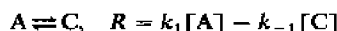
### 1. INTRODUCTION

Gas-liquid processes are frequently encountered in the chemical industry. Often the gas absorption rate is enhanced owing to chemical reaction(s) occurring in the liquid phase. A knowledge of this enhanced absorption is indispensable to come to an optimal design of the absorber. Therefore, much attention has been paid to the description and modelling of gas absorption accompanied by liquid reactions. These models are based on mass transfer theories like e.g. the film theory, Higbie penetration theory and the Danckwerts surface renewal theory (Danckwerts, 1970). Only in very few special cases can analytical solutions be obtained for the models, describing mass transfer accompanied by a chemical reaction [e.g. Olander (1960)], but mostly approximations or numerical techniques have to be used to solve the problem. The absorption rates derived with approximate models [e.g. van Krevelen and Hoftijzer (1948), Onda *et al.* (1970), DeCoursey (1982)] are only accurate under some specific conditions (Versteeg *et al.*, 1989). With numerical techniques the chosen model can be treated rigorously but resolution is, compared to the use of the approximate models, laborious and time-consuming. Once an absorption model has been solved by a numerical technique, results are easily and accurately obtained over a wide range of reaction and diffusion conditions. Recently, an extensive review in the field of modelling gas-liquid reactions has been presented by van Swaaij and Versteeg (1992).

However, if the reaction takes place in a small droplet with a finite chemical capacity the above-

mentioned models cannot be used because in these situations no bulk is present. Examples of reactors in which such processes take place are spray columns, (cyclone) spray scrubbers and liquid-liquid (reactive) extractors. Although the last one is not a gas-liquid process, there is no mathematical difference between the description of a gas-liquid process and that of a liquid-liquid process with two immiscible phases. Description of simultaneous mass transfer and reaction in a small liquid sphere should be instationary because of the finite capacity of the droplet. In the literature relatively little attention has been paid to the description of these instationary gas-liquid processes in small droplets. In case descriptions are given for reaction and mass transfer inside a droplet, attention is mainly focused on internally circulating or oscillating droplets. Due to this internal circulation or oscillation, mass transfer not only proceeds by diffusion but also by convection. The circulation in, or oscillation of, the particle occurs as a consequence of the friction of the sphere with the surrounding medium. Circulating droplets with an irreversible second-order reaction  $A + B \rightarrow \text{product(s)}$  have been studied by Brunson and Wellek (1971), Brounshtein *et al.* (1976) and Gürkan (1990). Brunson and Wellek (1971) also included results for a completely stagnant droplet. So far, no results are published for complex reversible reactions in stagnant liquid spheres. Only some limiting cases were analytically solved.

Crank (1976) presented an analytical solution for the simple reaction



in which A absorbs in a stagnant particle and C is immobile. Wu *et al.* (1976) treated the same problem

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by numerical inversion of Laplace transforms, but they did not compare their results with the analytical solution of Crank. Sada and Ameno (1973) derived an analytical solution for an instantaneous irreversible reaction  $A + B \rightarrow \text{product(s)}$  in a stagnant liquid film for equal diffusivities of components A and B. The description for a stagnant sphere can be obtained analogous to their derivation for a stagnant film. Some approximate solutions, based on a pseudo steady state for component A, can be taken from the literature about gas-solid reactions [see Froment and Bischoff (1990)]. The approximate models obtained for these reactions (e.g. shrinking core model) are of little practical importance for stagnant liquid spheres, because for gas-solid reactions reactant B is immobile.

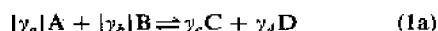
The description of a stagnant liquid sphere can also be applied to an inert porous particle which is filled with a liquid. When the particle is inert and fully impregnated with a reactive liquid, the description of diffusion and reaction is, apart from the introduction of a porosity and tortuosity factor, identical to that of diffusion and reaction in a stagnant liquid sphere.

This immobilization process offers interesting possibilities in gas treating as an alternative to the traditional gas-liquid contactors. By using small particles (e.g. 100–500  $\mu\text{m}$ ), a very large interfacial area can be created. The immobilization process is only meaningful for fast reactions which are normally mainly controlled by gas-phase transport and/or diffusional transport in the liquid phase. It possibly can be used for the purification of valuable components [e.g. separation of CO from synthesis gas with the Cosorb solution (Haasse, 1973)] or the (selective) removal of small amounts of (harmful) gases (e.g. removal of  $\text{H}_2\text{S}$  from natural gas with amine solutions). Instead of circulating the liquid from an absorber to a desorber, now the impregnated particles have to be circulated to obtain a continuous gas separation process. Reactors seeming to be suitable are, for example, fluidized beds, gas-solid trickle flow reactors and risers.

The immobilization of a liquid is already applied in steady-state catalytic processes, where the particles can be either fixed in a bed [e.g. Rao and Datta (1988)] or fluidized [e.g. Ohlrogge (1988)]. Also in various patents (Lutchko, 1973; Rouxguerraz *et al.*, 1980) the absorption of gases like COS,  $\text{H}_2\text{S}$  and  $\text{CO}_2$  into immobilized amine solutions was studied experimentally.

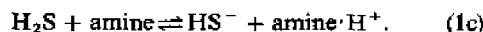
Before applying this new gas separation method important matters like the inertness of the carrier, evaporation of the liquid, the fluidization behaviour of the impregnated particles and absorption behaviour in an impregnated particle have to be studied theoretically as well as experimentally.

In this paper theoretical results for the gas-liquid reaction



(A is the absorbed component) with arbitrary kinetics in a stagnant liquid sphere or stagnant-liquid-filled

porous particle will be presented. The generalized reaction scheme (1a) makes it possible to investigate a wide variety of reactions: from a simple first-order irreversible reaction to a complex reversible reaction with arbitrary kinetics. The two reactions of particular interest are the Cosorb reaction (1b) and the  $\text{H}_2\text{S}$ -amine reaction (1c), which are both covered by the generalized reaction (1):



Furthermore, results will be presented when a second gas, E, absorbs simultaneously in the liquid-filled particle and consumes B, resulting in products C and F [reaction (2a)]. This occurs in the simultaneous absorption of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  into amine solutions, where, besides reaction (1b), the undesirable reaction between  $\text{CO}_2$  and an (for example, primary) amine takes place [reaction (2b)]:



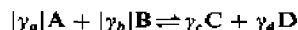
## 2. THEORY

### 2.1. Introduction

The theory for mass transfer accompanied by reactions of finite (Section 2.2) as well as infinite (Section 2.3) reaction rate in a stagnant-liquid-filled particle will be treated. The theory for instantaneous reactions is useful in deriving analytical solutions for some asymptotic situations. In Section 2.4 some remarks on the assumptions made in the present model are given.

### 2.2. Theory for mass transfer accompanied by reactions of finite rate

If reactant A absorbs in a stagnant liquid sphere, where it reacts with component B according to the reaction



$$\gamma_a \text{ and } \gamma_b \leq 0, \gamma_c \text{ and } \gamma_d \geq 0 \quad (1)$$

with the kinetics

$$R_1 = k_{a,m}[A]^a[B]^m - k_{p,e}[C]^p[D]^q$$

the non-stationary mass transfer and reaction in the droplet can, for each component, be described by

$$\frac{\partial[i]}{\partial t} = \frac{D_i}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial[i]}{\partial r} \right) + \gamma_i R_1 \quad i = A, B, C \text{ or } D. \quad (3a)$$

When the reaction proceeds in an inert porous particle filled with a stagnant liquid, relation (3a) transforms, after incorporation of porosity and tortuosity, into

$$e_p \frac{\partial[i]}{\partial t} = \frac{e_p D_i}{q r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial[i]}{\partial r} \right) + e_p \gamma_i R_1 \quad i = A, B, C \text{ or } D. \quad (3b)$$

The boundary and initial conditions for the liquid-filled particle are:

$$[i]_{r=0} = \text{constant}, \quad 0 \leq r \leq r_1, \quad i = A, B, C \text{ or } D \quad (4)$$

$$k_G \left( [A]_g - \frac{[A]_{r_1}}{m_a} \right) = D_a \frac{\varepsilon_p}{q} \frac{\partial [A]}{\partial r} \Big|_{r_1} \quad (\text{volatile component A}) \quad (5)$$

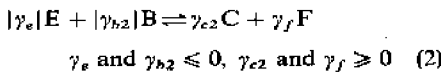
$$\frac{\partial [i]}{\partial r} \Big|_{r_1} = 0 \quad (\text{non-volatile components B, C and D}) \quad (6)$$

$$r^2 \frac{\partial [i]}{\partial r} \Big|_{r=0} = 0, \quad i = A, B, C \text{ or } D. \quad (7a)$$

Although relation (7a) gives the mathematically correct boundary condition, it is widely accepted to use eq. (7b) instead:

$$\frac{\partial [i]}{\partial r} \Big|_{r=0} = 0, \quad i = A, B, C \text{ or } D. \quad (7b)$$

If a second parallel reaction of finite rate occurs, as in the simultaneous absorption of  $H_2S$  and  $CO_2$  in amine solutions, which can be described by



and the reaction rate by

$$R_2 = k_{r,2}[E]^n[B]^n - k_{u,2}[C]^n[F]^n$$

the balances for components E and F are, by replacing  $R_1$  by  $R_2$ , equivalent to eq. (3b). The boundary conditions for the volatile component E are given by the same relations (5) and (7b) as for component A. The boundary conditions for component F are given by relations (6) and (7b).

For components B and C, eq. (3b) is extended with a second reaction term  $R_2$ :

$$\varepsilon_p \frac{\partial [i]}{\partial t} = \frac{\varepsilon_p D_i}{q} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [i]}{\partial r} \right) + \varepsilon_p \gamma_i R_1 + \varepsilon_p \gamma_{i2} R_2$$

$$i = B \text{ or } C. \quad (8)$$

The initial condition for each component is given by eq. (4).

### 2.3. Instantaneous reactions

If the reaction is instantaneous the reaction rate is infinite and, consequently, eq. (3b) cannot be used. However, the reaction rate in eq. (3b) can be eliminated for three of the components (e.g. A, B and D) by combining the balances of these components with the balance for the remaining component C. The result is

$$\gamma_c \frac{\partial [i]}{\partial t} - \gamma_i \frac{\partial [C]}{\partial t} = \gamma_c \frac{D_i}{q r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [i]}{\partial r} \right) - \gamma_i \frac{D_c}{q r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [C]}{\partial r} \right), \quad i = A, B \text{ or } D. \quad (9)$$

For instantaneous reactions, equilibrium is reached at any point and time within the particle, and the missing balance for component C is given by the equilibrium condition

$$K_1 = \frac{[C]^n [D]^n}{[A]^n [B]^n}. \quad (10)$$

For an instantaneous reaction the boundary conditions at  $r = r_1$  change as well. These can easily be derived from a mass balance over the particle. Only component A absorbs into the particle, while the other components are non-volatile. Therefore, the following conditions must be satisfied for the volatile component A and the non-volatile components B and D, respectively:

$$k_g 4\pi r_1^2 \left( [A]_g - \frac{[A]_{r_1}}{m_a} \right) = \varepsilon_p \int_0^{r_1} 4\pi r^2 \left( \frac{\partial [A]}{\partial t} + \frac{|\gamma_a|}{\gamma_c} \frac{\partial [C]}{\partial t} \right) \partial r \quad (11a)$$

and

$$0 = \varepsilon_p \int_0^{r_1} 4\pi r^2 \left( \frac{\partial [i]}{\partial t} - \frac{\gamma_i}{\gamma_c} \frac{\partial [C]}{\partial t} \right) \partial r$$

$$i = B \text{ or } D. \quad (12a)$$

Substituting relation (9) for the accumulation terms gives, for eq. (11a),

$$k_g 4\pi r_1^2 \left( [A]_g - \frac{[A]_{r_1}}{m_a} \right) = 4\pi \varepsilon_p \int_0^{r_1} \left[ \frac{D_a}{q} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [A]}{\partial r} \right) + \frac{|\gamma_a|}{\gamma_c} \frac{D_c}{q} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [C]}{\partial r} \right) \right] \partial r \quad (11b)$$

and relation (12a) transforms into

$$0 = \int_0^{r_1} \left[ D_i \frac{\partial}{\partial r} \left( r^2 \frac{\partial [i]}{\partial r} \right) - \frac{\gamma_i}{\gamma_c} D_c \frac{\partial}{\partial r} \left( r^2 \frac{\partial [C]}{\partial r} \right) \right] \partial r.$$

$$(12b)$$

After integration relation (11b) gives

$$k_g r_1^2 \left( [A]_g - \frac{[A]_{r_1}}{m_a} \right) = \varepsilon_p \left[ \frac{r^2 D_a}{q} \frac{\partial [A]}{\partial r} + \frac{|\gamma_a|}{\gamma_c} \frac{r^2 D_c}{q} \frac{\partial [C]}{\partial r} \right]_{r_1} \quad (11c)$$

and relation (12b) results in

$$0 = \left[ D_i r^2 \frac{\partial [i]}{\partial r} - \frac{\gamma_i}{\gamma_c} D_c r^2 \frac{\partial [C]}{\partial r} \right]_{r_1}$$

$$i = B \text{ or } D. \quad (12c)$$

Finally, the boundary conditions for an instantaneous reaction are obtained. For eq. (11c)

$$k_g \left( [A]_g - \frac{[A]_{r_1}}{m_a} \right) = D_a \frac{\varepsilon_p}{q} \frac{\partial [A]}{\partial r} \Big|_{r_1} + \frac{|\gamma_a|}{\gamma_c} D_c \frac{\varepsilon_p}{q} \frac{\partial [C]}{\partial r} \Big|_{r_1} \quad (11d)$$

is obtained, and eq. (12c) results in

$$D_i \frac{\partial [i]}{\partial r} \bigg|_{r_i} - \frac{\gamma_i}{\gamma_c} D_c \frac{\partial [C]}{\partial r} \bigg|_{r_i} = 0, \quad i = B \text{ or } D. \quad (12d)$$

The fourth boundary relation for the instantaneous reaction is given by the equilibrium condition (10).

#### 2.4. Assumptions in the present model

In the present absorption model for gas-liquid processes in stagnant-liquid-filled particles, isothermal conditions are assumed. This is justified only if small amounts of gas are absorbed and/or the reaction is not highly exothermic.

Moreover, constant non-coupled diffusion coefficients are supposed, as is the case for non-ionic solutions of low concentration. If ionic species are produced or consumed, the effect of the electrostatic gradient on the diffusivities has to be taken into account, like e.g. Glasscock and Rochelle (1989) and Littel *et al.* (1991) described. However, Littel *et al.* (1991) showed that the assumption of equal diffusion coefficients of the ionic products (total coupling) introduced only minor deviations compared to the situation in which the effect of the potential gradient on the decoupled ion diffusivities was taken into account. Therefore, in the present model electroneutrality was assured by giving all ionic species equal diffusivities.

### 3. NUMERICAL TREATMENT AND VERIFICATION

#### 3.1. Numerical treatment

In the numerical treatment of the model equations, the two reactions (1a) and (2a) of finite rates were taken into account. For components A, D, E and F eq. (3b) was used, and for components B and C, eq. (8). These equations and their appropriate initial and boundary conditions [relations (4)–(7)] were discretized according to the scheme proposed by Baker and Oliphant. This method has proven to give good results in the orthogonal system (Cornelisse *et al.*, 1980). Similar transformations as by Versteeg *et al.* (1989) were used to increase the grid density for short times and near the interface of the particle.

In the numerical treatment finite reaction rates are assumed, which does not cover the instantaneous reaction between  $H_2S$  and the amines. For instantaneous reactions, formally, eqs (9) and (10) with the boundary conditions (7b), (11d) and (12d) have to be discretized. However, instantaneous reactions can be simulated by giving the reaction rate constant a very high value. Although this treatment is mathematically not correct, minor errors were introduced with this approximation.

#### 3.2. Numerical verification and representation of the results

The results of the present absorption model were compared with analytical solutions for some asymptotic situations. These asymptotic situations are the (initially non-stationary) reaction  $A \rightarrow C$ , the reaction  $A \rightleftharpoons C$ , the instantaneous reaction  $A + B \rightleftharpoons C + D$  and the instantaneous reaction  $A \rightleftharpoons C$ .

For gas-liquid processes the enhancement factor is normally used to obtain an impression of the degree of enhanced absorption in the stationary situation. Owing to the absence of a stationary situation for both the physical and chemically enhanced flux in small stagnant-liquid-filled particles, usage of the enhancement factor seems meaningless. It may, for example, be possible that due to saturation the physical flux at a certain moment would be zero, while in the reactive situation saturation is not reached yet. This would result in infinite values for the enhancement factors. For this reason results are given in the form of dimensionless accumulations and fluxes as a function of time.

The contact times are varied between  $1 \times 10^{-5}$  and 100 s, which covers the process conditions encountered in cyclone spray scrubbers (Schrauwen, 1985), spray towers and that in liquid-liquid extraction. The contact time of the particles for the intended application ranges from  $\approx 0.1$  s in risers to more than 10 s in fluidized beds.

**3.2.1. Initially instationary irreversible first-order reaction  $A \rightarrow C$ .** The flux for the irreversible reaction  $A \rightarrow C$  in a sphere with  $R_1 = k_1[A]$  is (Crank, 1976)

$$J_a = \frac{2}{r_1} D_a m_a [A]_0 \sum_{n=1}^{\infty} \frac{k_1 r_1^2 + D_a n^2 \pi^2 \exp[-t(k_1 + D_a n^2 \pi^2 / r_1^2)]}{k_1 r_1^2 + D_a n^2 \pi^2} \quad (13)$$

After a certain period the flux becomes constant. In Table 1 the fluxes obtained with the numerical model and the analytical model are compared.

**3.2.2. Reversible reaction of finite rate.** Crank (1976) also presented a solution for the reaction  $A \rightleftharpoons C$  (C immobile) in a plane sheet with a constant surface concentration of A. Analogous to his derivation for a plane sheet, the following relation for the dimensionless total accumulation in a stagnant liquid

Table 1. Comparison of the fluxes for the numerical and the analytical models for an irreversible reaction of finite rate in a stagnant liquid sphere. Irreversible reaction  $A \rightarrow C$ :  $k_1 = 1000 \text{ s}^{-1}$ ,  $r_1 = 50 \text{ } \mu\text{m}$ ,  $\varepsilon_p = q = 1$ ,  $D_a = 1 \times 10^{-10} \text{ m}^2 \text{ s}^{-2}$ ,  $m_a = 1$ ,  $[A]_0 = 1 \text{ mol m}^{-3}$

Time (s)	Flux $\times 10^4 \text{ mol m}^{-2} \text{ s}^{-1}$	
	Numerical	Analytical
$1.563 \times 10^{-5}$	14.433	14.491
$6.400 \times 10^{-5}$	7.485	7.488
$1.250 \times 10^{-4}$	5.653	5.651
$1.000 \times 10^{-3}$	3.307	3.305
$8.000 \times 10^{-3}$	3.149	3.146
$1.563 \times 10^{-2}$	3.149	3.146
1.000	3.149	3.146

sphere is obtained:

$$\frac{A_t}{A_\infty} = 1 - \sum_{n=1}^{\infty} \sum_{i=1}^2 \frac{6(p_{ni}/k_{-1} + K + 1)^2 \exp(p_{ni}t)}{[(p_{ni}/k_{-1} + 1)^2 + K]r_1^2(K + 1)w_n^2} \quad (14a)$$

with

$$p_{n1} = [-k_1 - k_{-1} - Dw_n^2 + \sqrt{(k_1 + k_{-1} + Dw_n^2)^2 - 4k_{-1}Dw_n^2}]/2 \quad (14b)$$

$$p_{n2} = [-k_1 - k_{-1} - Dw_n^2 - \sqrt{(k_1 + k_{-1} + Dw_n^2)^2 - 4k_{-1}Dw_n^2}]/2 \quad (14c)$$

and

$$w_n^2 = \frac{n^2\pi^2}{r_1^2} \quad (14d)$$

$A_\infty$  gives the total amount of A accumulated in the liquid sphere at the end of the absorption process and equals

$$\begin{aligned} A_\infty &= V_{\text{sphere}}(m_a[A]_g + [C]_{\text{eq}}) \\ &= V_{\text{sphere}}(m_a[A]_g + Km_a[A]_g). \end{aligned} \quad (14e)$$

In Table 2 a comparison of the dimensionless total accumulation of A for the present numerical model and the analytical model [given by eq. (14a)] is presented.

**3.2.3. Instantaneous reversible reaction with equal diffusivities.** If the reaction rate for the reaction  $|\gamma_a|A + |\gamma_b|B \rightleftharpoons \gamma_c C + \gamma_d D$  can be considered instantaneous with respect to mass transfer and if the diffusion coefficients of the reactants and products are equal, an analytical solution can be obtained. The combined mass balances for component C with, respectively, B and D in relation (9) disappear, because for equal diffusivities

$$\frac{\partial[i]}{\partial r} = \frac{\gamma_i}{\gamma_c} \frac{\partial[C]}{\partial r}, \quad i = B \text{ or } D. \quad (15a)$$

This means that at every point in the particle the concentrations of B and D can be written as a function of [C] according to

$$[B] = [B]_0 - \frac{|\gamma_b|}{\gamma_c} [C] \quad (15b)$$

and

$$[D] = \frac{\gamma_d}{\gamma_c} [C]. \quad (15c)$$

Because [B] and [D] are only a function of [C], the concentration of A can, with the aid of the equilibrium constant in eq. (10), also be written as a function of [C]:

$$[A]^n = \frac{[C]^p [D]^q}{K_1 [B]^m} = \frac{[C]^p \left( \frac{\gamma_d}{\gamma_c} [C] \right)^q}{K_1 \left( [B]_0 - \frac{|\gamma_b|}{\gamma_c} [C] \right)^m} = f[C]. \quad (16a)$$

Therefore, the concentration of A can be written as

$$[A] = (f[C])^{1/n}. \quad (16b)$$

Equation (16b) can be substituted in the combined diffusion equation for components A and C [eq. (9)]. This means that an instantaneous reaction with equal diffusivities of reactants and products is described by the following relation:

$$\begin{aligned} &\frac{\partial[\gamma_c f([C])^{1/n} + |\gamma_a|[C]]}{\partial t} \\ &= \frac{D_c}{qr^2} \frac{\partial}{\partial r} \left\{ r^2 \frac{\partial[\gamma_c f([C])^{1/n} + |\gamma_a|[C]]}{\partial r} \right\}. \end{aligned} \quad (17a)$$

Dividing eq. (17a) by  $\gamma_c$  and introducing the variable [P] which is defined as

$$[P] = [A] + \frac{|\gamma_a|}{\gamma_c} [C] = f[C]^{1/n} + \frac{|\gamma_a|}{\gamma_c} [C] \quad (18)$$

transforms relation (17a) in the diffusion equation for a sphere:

$$\frac{\partial[P]}{\partial t} = \frac{D_c}{qr^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial[P]}{\partial r} \right). \quad (17b)$$

The analytical solution for this diffusion equation in terms of the dimensionless total accumulation is (Crank, 1976)

$$\frac{[P]_t}{[P]_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-D_c n^2 \pi^2 t / (r_1^2 q)]. \quad (19a)$$

$[P]_\infty$  equals the concentration of P in the liquid at the end of the absorption process and can be written as

$$[P]_\infty = m[A]_g + |\gamma_a|[C]_{\text{eq}}/\gamma_c. \quad (19b)$$

In relation (19b)  $[C]_{\text{eq}}$  represents the concentration of C in the liquid at the end of the absorption process according to the equilibrium constant  $K_1$  [eq. (10)]. In Table 3 a comparison between the present numer-

Table 2. Comparison of the dimensionless total accumulation for the numerical and the analytical models for a reversible reaction of finite rate. Reversible reaction  $A \rightleftharpoons C$ : C is immobile,  $D_a = 1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ,  $k_1 = 1000 \text{ s}^{-1}$ ,  $k_{-1} = 100 \text{ s}^{-1}$ ,  $r_1 = 50 \text{ } \mu\text{m}$ ,  $\varepsilon_p = q = 1$ ,  $m_a = 1$ ,  $[A]_g = 1 \text{ mol m}^{-3}$

Time (s)	Dimensionless total accumulation	
	Numerical	Analytical
0.0216	0.02589	0.02583
0.100	0.06198	0.06193
0.410	0.1255	0.1254
1.217	0.2115	0.2115
7.951	0.4887	0.4887
25.00	0.7478	0.7478
100.0	0.9832	0.9832

Table 3. Comparison of the dimensionless total accumulation for the numerical and the analytical models for the reversible instantaneous reaction  $A + B \rightleftharpoons C + D$ . Instantaneous reaction simulated with  $k_1 = 1 \times 10^{10} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ; all diffusion coefficients are  $1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ;  $K = 100$ ; no gas-phase resistance;  $r_1 = 50 \text{ } \mu\text{m}$ ;  $\epsilon_p = q = 1$ ;  $m_a = 1$ ;  $[A]_p = 1 \text{ mol m}^{-3}$

Time (s)	Dimensionless total accumulation	
	Numerical	Analytical
$8.00 \times 10^{-5}$	0.00622	0.00605
$2.70 \times 10^{-4}$	0.01120	0.01110
$6.40 \times 10^{-4}$	0.01714	0.01705
$2.20 \times 10^{-2}$	0.09773	0.09771
$8.00 \times 10^{-2}$	0.1819	0.1819
$4.67 \times 10^{-1}$	0.4064	0.4065
1.5315	0.6540	0.6541
4.135	0.8804	0.8808

ical model and the analytical model [eq. (19a)] is presented.

According to eq. (19a) the dimensionless total accumulations at every moment are identical for both the unreactive- (only physical absorption) and reactive-liquid-filled particle. Therefore, this is, in fact, the only situation in which the concept of the enhancement factor,  $E_a$ , can be used. The flux for the reactive-liquid-filled particle is expressed by

$$J_{a, \text{reactive}} = J_{a, \text{physical}} E_a$$

$$= J_{a, \text{physical}} \left( 1 + \frac{|\gamma_a| [C]_{eq}}{\gamma_c m_a [A]_p} \right) \quad (20)$$

where  $J_{a, \text{physical}}$  represents the physical flux into the sphere at a certain moment. This flux can be derived from eq. (13) if  $k_1 = 0$  and is, after incorporation of  $\epsilon_p$  and  $q$ , given by

$$J_{a, \text{physical}} = \frac{2}{r_1} \epsilon_p \frac{D_a}{q} m_a [A]_p \sum_{n=1}^{\infty} e^{-D_a n^2 \pi^2 / (r_1^2 q)} \quad (21a)$$

For short times the particle can be considered as a semi-infinite medium, and the flux can be described by the more simple expression (21b):

$$J_{a, \text{physical}} = \epsilon_p \sqrt{\frac{D_a}{\pi q t}} (m_a [A]_p) \quad (21b)$$

**3.2.4. Instantaneous reversible reaction with unequal diffusivities.** If the diffusion coefficients of the reactants and products are not equal, an analytical solution for the instantaneous reversible reaction  $\gamma_a A \rightleftharpoons \gamma_c C$  can be derived if the equilibrium constant can be written as  $[C] = K[A]$ . Substituting  $[C] = K[A]$  in eq. (9) gives, after rearrangement, the diffusion equation in a sphere:

$$\frac{\partial [A]}{\partial t} = \left[ \frac{\gamma_c D_a + |\gamma_a| K D_c}{q(\gamma_c + |\gamma_a| K)} \right] \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [A]}{\partial r} \right) \quad (22)$$

The diffusion coefficient in eq. (22) is a weighted average of the diffusivities of A and C and can be expressed by

$$D_m = \frac{\gamma_c}{\gamma_c + |\gamma_a| K} \frac{D_a}{q} + \frac{|\gamma_a| K}{\gamma_c + |\gamma_a| K} \frac{D_c}{q} \quad (23)$$

The analytical solution in terms of the dimensionless total accumulation arises by replacing  $D_c/q$  by  $D_m$  in eq. (19a).

In Table 4 a comparison between the present numerical model and the analytical model [given by eqs (19a) and (23)] is presented.

**3.2.5. Validity of the numerical model.** From Tables 1–4 it can be concluded that the present numerical model gives accurate results over a wide range of reaction conditions. Approximating instantaneous reactions with high reaction rate constants introduces only small deviations in comparison with the analytical model.

#### 4. NUMERICAL SIMULATIONS FOR A SINGLE REVERSIBLE REACTION

##### 4.1. Introduction

In this section numerical results for the simultaneous diffusion and reaction are presented, if gas A absorbs in a liquid-filled particle or in a liquid sphere where reaction (1a) takes place. Reactions with both infinite (Section 4.2) and finite (Section 4.3) reaction rates will be treated. As discussed previously in Section 3.1, results are given in terms of fluxes and dimensionless total accumulations as a function of time. The dimensionless total accumulation in the figures corresponds to the total amount of component A transferred to the particle divided by the amount of

Table 4. Comparison of the dimensionless total accumulation for the present numerical model and the analytical model for an instantaneous first-order reaction with unequal diffusivities of A and C. Instantaneous reaction  $A \rightleftharpoons C$ ;  $K = 1$ ; instantaneous reaction simulated with  $k_1 = 1 \times 10^{10} \text{ s}^{-1}$ ;  $m_a = 1$ ;  $[A]_p = 1 \text{ mol m}^{-3}$ ;  $r_1 = 100 \text{ } \mu\text{m}$ ;  $\epsilon_p = q = 1$ ;  $D_a = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ;  $D_c = 1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ; no gas-phase resistance

Time (s)	Dimensionless total accumulation	
	Numerical	Analytical
$1.2500 \times 10^{-3}$	0.01241	0.01245
$6.1413 \times 10^{-3}$	0.02723	0.02748
$8.0000 \times 10^{-2}$	0.09724	0.09731
$2.7000 \times 10^{-1}$	0.17467	0.17474
1.2500	0.35406	0.35413
5.1200	0.63203	0.63208
10.000	0.79039	0.79043

A transferred to the particle at the end of the absorption process, and equals

$$\frac{A_t}{A_\infty} = \frac{\int_0^{r_1} \varepsilon_p 4\pi r^2 \left( [A] + \frac{|\gamma_a|}{\gamma_c} [C] \right)_{t=t} dr}{\int_0^{r_1} \varepsilon_p 4\pi r^2 \left( [A] + \frac{|\gamma_a|}{\gamma_c} [C] \right)_{t=\infty} dr} = \frac{\int_0^{r_1} \varepsilon_p 4\pi r^2 \left( [A] + \frac{|\gamma_a|}{\gamma_c} [C] \right)_{t=t} dr}{\varepsilon_p \frac{4}{3} \pi r_1^3 \left( m_a [A]_g + \frac{|\gamma_a|}{\gamma_c} [C]_{eq} \right)} \quad (24)$$

This accumulation term was calculated by numerical integration in the particle.

#### 4.2. Numerical simulations of single instantaneous reactions

As already mentioned in Section 3.2.3 the description of absorption accompanied by an instantaneous reaction can be solved analytically if the diffusivities of all components are equal and the gas-phase resistance is negligible [eq. (19a)]. However, if the diffusivities are unequal an analytical solution can be derived only for the instantaneous reversible reaction  $|\gamma_a|A \rightleftharpoons \gamma_c C$  (see Section 3.2.4). The analytical expression for the combined diffusion coefficient,  $D_m$  [relation (23)], can be rewritten in the following form:

$$D_m = \frac{\gamma_c m_a [A]_g}{\gamma_c m_a [A]_g + |\gamma_a| [C]_{eq}} \frac{D_a}{q} + \frac{|\gamma_a| [C]_{eq}}{\gamma_c m_a [A]_g + |\gamma_a| [C]_{eq}} \frac{D_c}{q} \quad (25)$$

In gas-liquid processes the physical accumulation of component A ( $m_a [A]_g$ ), compared to the accumulation of component C ( $[C]_{eq}$ ), normally small and the diffusivities of components A and C are of the same order of magnitude. This means that the contribution of the first term on the right-hand side of relation (25) is much smaller than the second one, and that the diffusion coefficient,  $D_m$ , is mainly determined by the diffusivity of component C.

If reaction (1a) can be regarded as instantaneous and  $D_a \neq D_b = D_c = D_d$  no analytical solution can be derived for the dimensionless total accumulation. However, for high initial B concentrations ( $[B]_0$ ) and high equilibrium constants the concentration of  $[C]_{eq}$  will exceed the amount of physically absorbed A, and an approximation can be derived. As already demonstrated for the reaction  $\gamma_a A \rightleftharpoons \gamma_c C$  the dimensionless total accumulation is, for the condition  $[C]_{eq} \gg m_a [A]_g$ , mainly determined by the diffusivity of component C. For this reason the use of eq. (25) is suggested if reaction (1a) is instantaneous and  $D_a \neq D_b = D_c = D_d$ . In this way, an approximation for the dimensionless total accumulation can be obtained by replacing  $D_c/q$  in relation (19a) by eq. (25). As can be expected, this method gives accurate results if  $[C]_{eq} \gg m_a [A]_g$ , which is illustrated in Fig. 1. However, deviations are introduced if the contribution of

both terms in eq. (25) is comparable (see Fig. 2). In the particular example in Fig. 2 the influence of the diffusivity of component A is underestimated. However, for gas-liquid processes, normally,  $[C]_{eq} \gg m_a [A]_g$ , and the use of eq. (25) in relation (19a) will give accurate results for the dimensionless total accumulations.

With increasing gas-phase mass transfer resistance the importance of the diffusivities of the reactants and products on the dimensionless total accumulation decreases. This phenomenon is illustrated in Fig. 3. For decreasing  $k_g$  the saturation time increases, while the curves for the various diffusivities (especially at low liquid loadings) approach each other. For reactions with an increasing equilibrium constant as well as initial B concentration,  $[C]_{eq}$  will increase and the

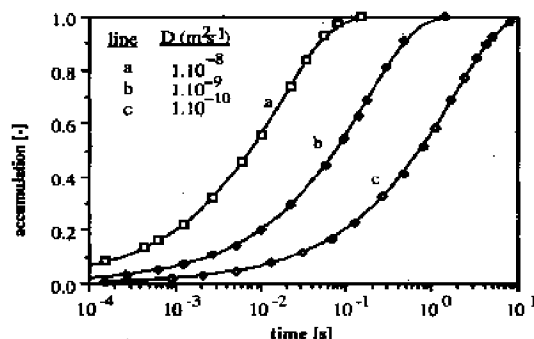


Fig. 1. Influence of diffusivities on the dimensionless total accumulation for an instantaneous reaction  $A + B \rightleftharpoons C + D$  in a liquid droplet:  $K = 100$ ;  $r_1 = 50 \mu\text{m}$ ;  $m_a = 1$ ;  $[A]_g = 1 \text{ mol m}^{-3}$ ;  $D_a = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ;  $[B]_0 = 1000 \text{ mol m}^{-3}$ ;  $[C]_{eq} = 270.2 \text{ mol m}^{-3}$ ;  $\varepsilon_p = q = 1$ ; no gas-phase resistance. Diffusion coefficients of B, C and D are equal, and varied between  $1 \times 10^{-8}$  and  $1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . Continuous line represents numerical results; points demonstrate the approximation with eqs (19a) and (25).

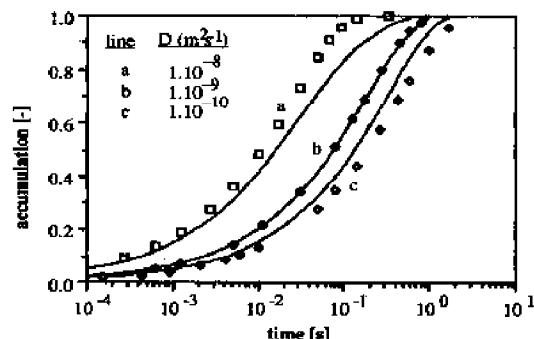


Fig. 2. Influence of diffusivities on the dimensionless total accumulation for an instantaneous reaction  $A + B \rightleftharpoons C + D$  in a liquid droplet:  $K = 100$ ;  $r_1 = 50 \mu\text{m}$ ;  $m_a = 1$ ;  $[A]_g = 1 \text{ mol m}^{-3}$ ;  $D_a = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ;  $[B]_0 = 2 \text{ mol m}^{-3}$ ;  $[C]_{eq} = 1.961 \text{ mol m}^{-3}$ ;  $\varepsilon_p = q = 1$ ; no gas-phase resistance. Diffusion coefficients of B, C and D are equal, and varied between  $1 \times 10^{-8}$  and  $1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . Continuous line represents numerical results; points demonstrate the approximation with eqs (19a) and (25).



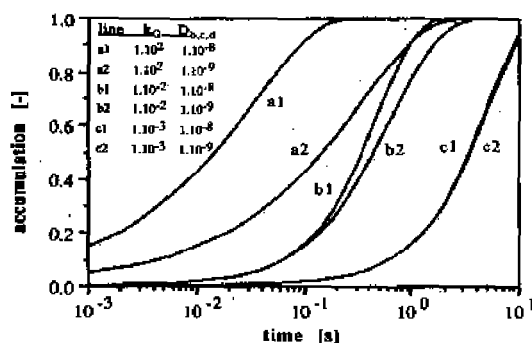


Fig. 3. Effect of  $k_g$  ( $\text{m s}^{-1}$ ) on the dimensionless total accumulation for the instantaneous reaction  $A + B \rightleftharpoons C + D$  in a liquid-impregnated particle:  $K = 500$ ;  $r_1 = 50 \mu\text{m}$ ;  $m_a = 1$ ;  $[A]_g = 1 \text{ mol m}^{-3}$ ;  $D_a = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ;  $[B]_0 = 2000 \text{ mol m}^{-3}$ ;  $[C]_{eq} = 780.78 \text{ mol m}^{-3}$ ;  $\varepsilon_p = 0.5$ ;  $q = 2$ . Diffusion coefficients of B, C and D are equal, and varied between  $1 \times 10^{-9}$  and  $1 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ .  $k_g$  is varied between 100 (no gas-phase resistance),  $1 \times 10^{-2}$  and  $1 \times 10^{-3} \text{ m s}^{-1}$ .

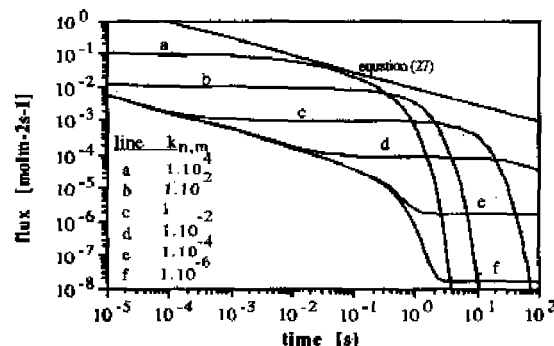


Fig. 4. Influence of the reaction rate constant  $k_{n,m}$  ( $\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) on the fluxes for the reaction  $A + B \rightleftharpoons C + D$  in a liquid sphere:  $K = 1 \text{ m}^3 \text{ mol}^{-1}$ ;  $r_1 = 50 \mu\text{m}$ ;  $m_a = 1$ ;  $[A]_g = 1 \text{ mol m}^{-3}$ ; all diffusion coefficients  $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ;  $[B]_0 = 1000 \text{ mol m}^{-3}$ ;  $[C]_{eq} = 500 \text{ mol m}^{-3}$ ;  $\varepsilon_p = q = 1$ ; no gas-phase resistance.

influence of the gas-phase resistance will increase as well.

#### 4.3. Numerical simulations for single reactions with finite reaction rate constants

If the reaction rate is finite only in the situation for very slow reactions a rather trivial approximate solution of a homogeneous reaction in the liquid-filled particle or liquid sphere can be derived. For other process conditions no generalized solution can be obtained. However, various absorption regimes can be recognized in the time-flux diagram. Examples of such time-flux diagrams and their corresponding time-accumulation graphs for some arbitrary reactions are given in Figs 4–7 and 8–11, respectively. Figures 4 and 5 give, apart from the diffusivities of B and C, results for the same process conditions. The forms of the time-flux curves are similar to the figures

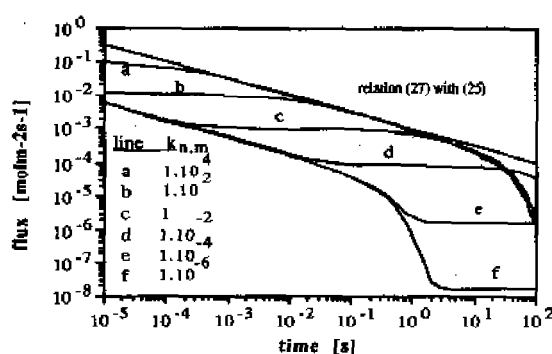


Fig. 5. Effect of the reaction rate constant  $k_{n,m}$  ( $\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) on the fluxes for the reaction  $A + B \rightleftharpoons C + D$  in a liquid sphere:  $K = 1 \text{ m}^3 \text{ mol}^{-1}$ ;  $r_1 = 50 \mu\text{m}$ ;  $m_a = 1$ ;  $[A]_g = 1 \text{ mol m}^{-3}$ ;  $D_a = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ;  $D_{B,C,D} = 1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ;  $[B]_0 = 1000 \text{ mol m}^{-3}$ ;  $[C]_{eq} = 500 \text{ mol m}^{-3}$ ;  $\varepsilon_p = q = 1$ ; no gas-phase resistance.

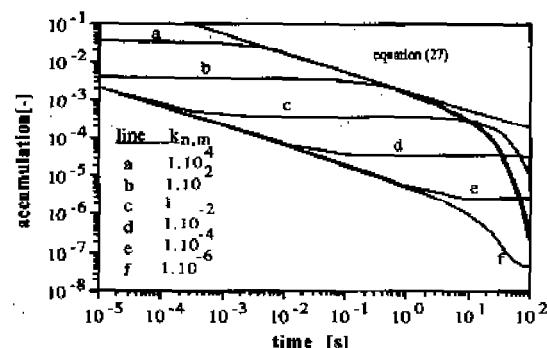


Fig. 6. Effect of the reaction rate constant  $k_{n,m}$  ( $\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) on the fluxes for the reaction  $A + B \rightleftharpoons C + D$  in a liquid-impregnated particle:  $K = 100$ ;  $r_1 = 250 \mu\text{m}$ ;  $m_a = 1$ ;  $[A]_g = 1 \text{ mol m}^{-3}$ ; all diffusion coefficients  $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ;  $[B]_0 = 1000 \text{ mol m}^{-3}$ ;  $[C]_{eq} = 270.2 \text{ mol m}^{-3}$ ;  $\varepsilon_p = 0.5$ ;  $q = 2$ ; no gas-phase limitation.

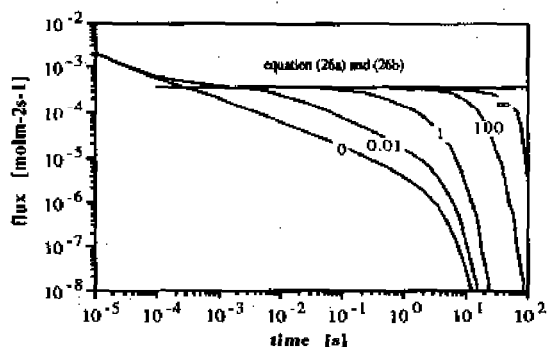


Fig. 7. Influence of the equilibrium constant  $K_1$  on the fluxes for the reaction  $A + B \rightleftharpoons C + D$  in a liquid-impregnated particle:  $K = 0$  (no reaction), 0.01, 1, 100,  $\infty$ ;  $r_1 = 100 \mu\text{m}$ ;  $m_a = 1$ ;  $[A]_g = 1 \text{ mol m}^{-3}$ ; all diffusion coefficients  $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ;  $[B]_0 = 1000 \text{ mol m}^{-3}$ ;  $[C]_{eq}$  is, respectively, 0, 3.157, 31.126, 270.2, 1000  $\text{mol m}^{-3}$ ;  $k_{1,1} = 1 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ;  $\varepsilon_p = 0.5$ ;  $q = 2$ ; no gas-phase limitation.

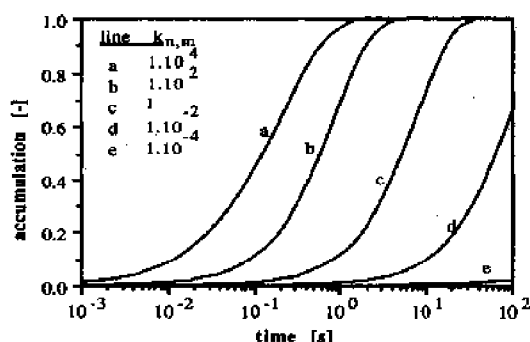


Fig. 8. Influence of the reaction rate constant  $k_{n,m}$  (m<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) on the dimensionless total accumulation corresponding to the conditions mentioned in the caption of Fig. 4.

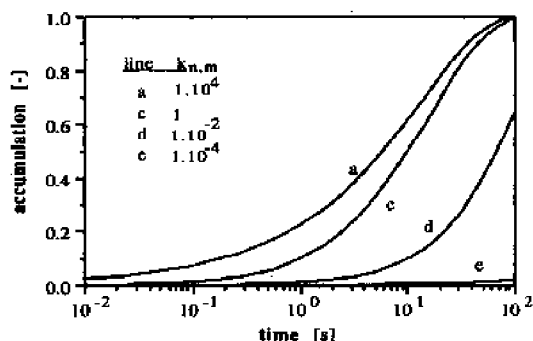


Fig. 9. Influence of the reaction rate constant  $k_{n,m}$  (m<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) on the dimensionless total accumulation corresponding to the conditions mentioned in the caption of Fig. 5.

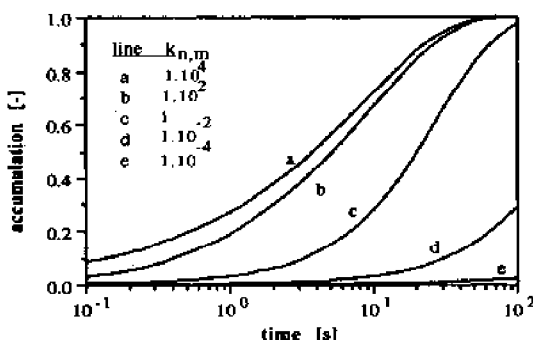


Fig. 10. Effect of the reaction rate constant  $k_{n,m}$  (m<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) on the dimensionless total accumulation corresponding to the conditions mentioned in the caption of Fig. 6.

given by Wu *et al.* (1976) for the reaction  $A \rightleftharpoons C$  (C immobile).

The first region of absorption is described by the physical flux into a liquid-filled particle and expressed by eq. (21a). For short times, relation (21a) or (21b)

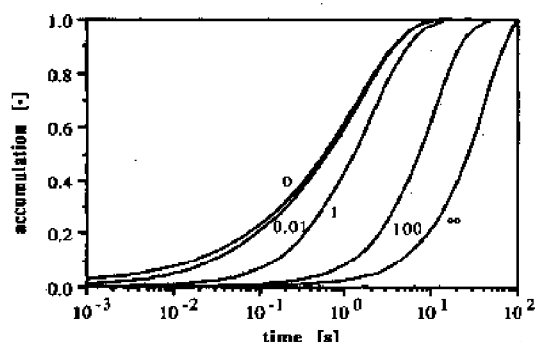


Fig. 11. Influence of the equilibrium value  $K_1$  on the dimensionless total accumulation corresponding to the conditions mentioned in the caption of Fig. 7.

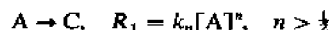
gives, in a double logarithm figure of the flux against the time, a straight line, which is independent of the particle radius. If the particle saturates with component A, the flux calculated by relation (21a) reduces substantially. This saturation moment increases with the radius of the liquid-filled particles.

After some time the physical flux becomes of the same order of magnitude as the reaction rate, and a plateau is reached. The plateau flux can, for a first-order reaction in A, be approximated by the relation for the stationary flux into a sphere where a first-order irreversible reaction takes place. Assuming a pseudo-first-order reaction of A, the approximate flux is, with incorporation of  $\varepsilon_p$  and  $q$ , described by

$$J_a = k_{1,m}[B]_0^m \varepsilon_p m_a [A]_a \frac{r_1}{3} \frac{\tanh \phi'}{\phi'} \quad (26a)$$

$$\phi' = \frac{r_1}{3} \sqrt{\frac{k_{1,m}[B]_0^m q}{D_a}} \quad (26b)$$

Bischoff (1965) gave an approximation for the stationary flux for the irreversible reaction



but the stationary fluxes calculated by the approximation gave, for  $n = 2$ , fluxes which differed by more than 50% from the numerically calculated fluxes. Consequently, only the plateau flux for a reaction first-order in A can be approximated reasonably well with eqs (26a) and (26b) (see Figs 7 and 11). For fast reactions  $\tanh \phi' \approx 1$ , indicating that the plateau flux is independent of the particle radius, while for very slow reactions  $\tanh \phi' \approx \phi'$ , meaning that the flux depends linearly on  $r_1$ . The continuation of the flux line is, among others, determined by the diffusivities of the components B, C and D, the initial concentration of B ( $[B]_0$ ), the particle radius and the equilibrium constant. In Figs 7 and 11 the influence of the equilibrium constant is shown. From these figures it can be seen that for increasing equilibrium constants the flux remains on the plateau for a longer period, and, as

a result, the time to reach complete conversion increases. The increased saturation time is due to the fact that the plateau flux for all equilibrium constants is identical, while the absorption capacity increases with increasing equilibrium constant.

If no severe diffusion resistance of components B, C and D occurs, the plateau flux gradually decreases until the particle is completely saturated (Fig. 4). If, however, diffusion limitation of B, C and D takes place, a rather abrupt change to an instantaneous reaction regime can be observed (Fig. 5). In this region the reaction rate is not important and above a certain asymptotic rate constant the fluxes are almost equal. When saturation takes place the flux drops from this line and decreases to zero. The instantaneous regime can, for equal diffusivities, be approximated by the flux into a flat semi-infinite medium:

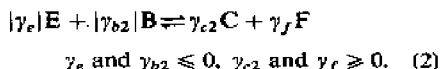
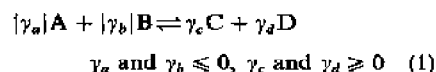
$$J_a = \varepsilon_p \sqrt{\frac{D_a}{\pi q t}} \left( m_a [A]_g + \frac{|\gamma_a|}{\gamma_c} [C]_{eq} \right). \quad (27)$$

This line can be regarded as the upper limit for the flux at the instantaneous regime. For unequal diffusivities the approximation for  $D_m$  as suggested in relation (25) can be used in eq. (27). The use of these relations is illustrated in Figs 4–6. In Fig. 4 notable diffusion resistance occurs only for the fastest reaction, while in Fig. 5 diffusion limitation occurs for reactions with a rate constant above  $1 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . In Fig. 6 diffusion limitation is observed for reactions with a reaction constant above  $100 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . As already mentioned in Section 4.2, eq. (25) gives accurate results if the diffusivities of A and C are of the same order of magnitude and  $[C]_{eq} \gg m_a [A]_g$ . In the instantaneous regime the fluxes calculated by relations (25) and (27) differ, for the conditions studied, only a few percent from the numerically calculated fluxes.

## 5. SIMULTANEOUS ABSORPTION OF TWO GASES

### 5.1. Introduction

In the simultaneous absorption of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  into aqueous amine solutions, both the desirable reaction (1c) and undesirable reaction (2b) take place. These two reactions are given schematically by



In reality, the reaction scheme for this special case is much more complicated, as represented by reactions (1a) and (2a); however, Littel *et al.* (1991) showed that using the complicated and the simplified reaction scheme gave, for a model based on the Higbie penetration theory, nearly identical results. Therefore, the simplified reaction scheme, given by the two reactions (1a) and (2a), was used in the present study.

In Section 5.2 several examples will be given for the simultaneous absorption of two reactive gases, of

which the desirable gas, A, reacts instantaneously, and the other one, E, with a finite rate. Based on these results, a particular example for the absorption of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  in a particle impregnated with methyl diethanol amine (MDEA) will be given.

In the simulation results, the dimensionless total accumulation for components A and E is defined similar to eq. (24), and gives the amount of A (or E) transferred to the particle divided by the maximum amount of A (or E) that can be absorbed by the liquid-filled particle. The denominator in relation (24) is defined as if one reaction takes place; therefore, the dimensionless total accumulation (for both A and E) can never exceed unity. The equilibrium concentrations given in the captions are also calculated as if one reaction takes place. In Figs 12–17 the accumulation curves for both A and E are given in the same figure. The number following the gas indicates the value of the parameter which is varied.

### 5.2. Simulation results for the simultaneous absorption of two gases

It will be obvious that the equilibrium constants determine the concentrations at the end of the absorption process. However, if the first reaction is fast, or even instantaneous (as in the examples treated here), and the second reaction slow, the dimensionless total accumulation of component A in the particle can exceed the final equilibrium accumulation. This is illustrated in Fig. 12, where the equilibrium constant favours the second reaction, but, nevertheless, the dimensionless total accumulation of component A reaches, for a slow parallel reaction, a value as if the second reaction does not occur. With increasing reaction rate constant of the second reaction, the maximum accumulation of A diminishes and shifts to lower contact times. However, the maximum amount of A transferred to the particle is, even for the fastest

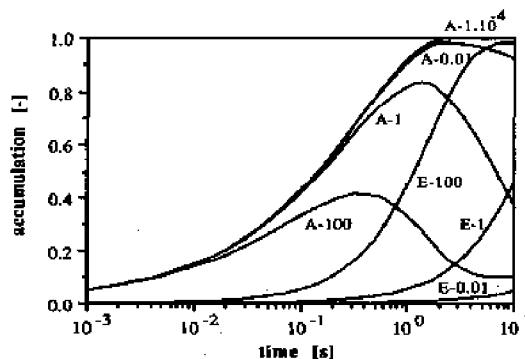


Fig. 12. Effect of the reaction rate constant  $k_{r,2}$  ( $\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) of reaction (2a) on the simultaneous absorption of two gases A and E in a liquid-impregnated particle:  $r_1 = 50 \mu\text{m}$ ;  $K_1 = 50$ ;  $K_2 = 2000$ ; reaction (1a) is instantaneous;  $[B]_0 = 1000 \text{ mol m}^{-3}$ ;  $m_a = 1$ ;  $[A]_g = 1 \text{ mol m}^{-3}$ ;  $m_e = 1$ ;  $[E]_g = 1 \text{ mol m}^{-3}$ ;  $[D]_{eq} = 200 \text{ mol m}^{-3}$ ;  $[F]_{eq} = 732.05 \text{ mol m}^{-3}$ ;  $\varepsilon_p = 0.5$ ;  $q = 2$ ; all diffusivities  $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ; no gas-phase resistance.

reaction under consideration, considerably higher than the amount accumulated at the end of the absorption process. In Fig. 12, for the fastest parallel reaction only, equilibrium is reached within the given time scale. As can be seen from Fig. 13 an increasing equilibrium constant for the second reaction has a similar effect as an increase of the reaction rate constant for the second reaction. If the desirable reaction has an infinite reaction rate and the undesirable reaction a finite reaction rate, the particle dimensions should be as small as possible in order to increase the maximum capacity for the desirable component and reduce the time at which this capacity is reached (see Fig. 14). After reaching a maximum, desorption of component A takes place, which is illustrated in Fig. 15 for the two situations shown in Figs 13 and 14. The influence of  $k_g$  on the absorption behaviour of the two

gases is illustrated in Fig. 16. From this figure it can be concluded that a gas-phase resistance has a negative effect on the maximum absorption capacity of A and the time at which this maximum is reached.

### 5.3. Simultaneous absorption of $H_2S$ and $CO_2$ in a MDEA-impregnated particle

From the figures in Section 5.2 it can be concluded that small particles and a slow reaction of  $CO_2$  with an amine contribute to an efficient use of the amine for the selective absorption of the instantaneously reacting  $H_2S$ . For this reason, aqueous MDEA solutions impregnated in particles with a radius of

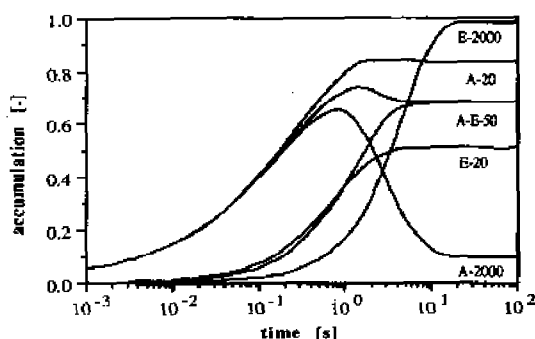


Fig. 13. Effect of the equilibrium constant  $K_2$  of reaction (2a) on the simultaneous absorption of two gases A and E in a liquid-impregnated particle:  $r_1 = 50 \mu m$ ;  $K_1 = 50$ ; reaction (1a) is instantaneous;  $k_{r,s} = 10 m^3 mol^{-1} s^{-1}$ ;  $[B]_0 = 1000 mol m^{-3}$ ;  $m_a = 1$ ;  $[A]_g = 1 mol m^{-3}$ ;  $m_e = 1$ ;  $[E]_g = 1 mol m^{-3}$ ;  $[D]_{eq} = 200 mol m^{-3}$ ;  $[F]_{eq} = 131.77, 200, 732.05 mol m^{-3}$ ;  $\epsilon_p = 0.5$ ;  $q = 2$ ; all diffusivities  $1 \times 10^{-9} m^2 s^{-1}$ ; no gas-phase resistance.

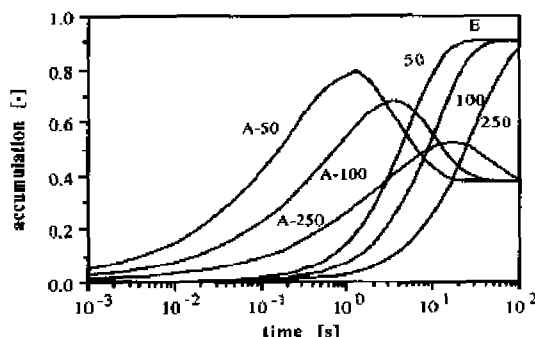


Fig. 14. Influence of the particle radius ( $\mu m$ ) on the simultaneous absorption of two gases A and E in a liquid-impregnated particle:  $K_1 = 20$ ;  $K_2 = 100$ ; reaction (1a) is instantaneous;  $k_{r,s} = 1 m^3 mol^{-1} s^{-1}$ ;  $m_a = 1$ ;  $[A]_g = 1 mol m^{-3}$ ;  $m_e = 1$ ;  $[E]_g = 1 mol m^{-3}$ ;  $[B]_0 = 1000 mol m^{-3}$ ;  $[D]_{eq} = 131.77$ ;  $[F]_{eq} = 270.2 mol m^{-3}$ ;  $\epsilon_p = 0.5$ ;  $q = 2$ ; all diffusivities  $1 \times 10^{-9} m^2 s^{-1}$ ; no gas-phase resistance.

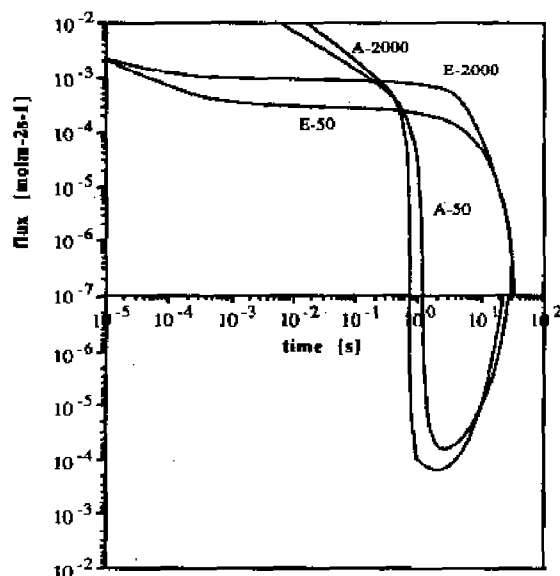


Fig. 15. Fluxes corresponding to situation A-2000, E-2000, A-50 and E-50 from, respectively, Figs 13 and 14.

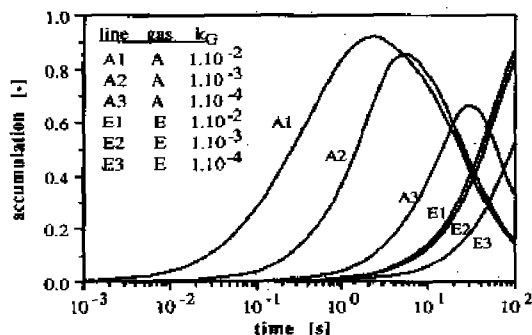


Fig. 16. Effect of gas-phase mass transfer  $k_g$  ( $m s^{-1}$ ) on the simultaneous absorption of two gases A and E in a liquid-impregnated particle:  $K_1 = 50$ ;  $K_2 = 2000$ ;  $r_1 = 50 \mu m$ ; reaction (1a) is instantaneous;  $k_{r,s} = 0.1 m^3 mol^{-1} s^{-1}$ ;  $m_a = 1$ ;  $[A]_g = 1 mol m^{-3}$ ;  $m_e = 1$ ;  $[E]_g = 1 mol m^{-3}$ ;  $[B]_0 = 2000 mol m^{-3}$ ;  $[D]_{eq} = 292.21$ ;  $[F]_{eq} = 1236.07 mol m^{-3}$ ; all diffusivities  $1 \times 10^{-9} m^2 s^{-1}$ ;  $\epsilon_p = 0.5$ ;  $q = 2$ ;  $k_g$  is varied from  $1 \times 10^{-2}$  to  $1 \times 10^{-4} m s^{-1}$ .

Table 5. Data for the MDEA-H<sub>2</sub>S-CO<sub>2</sub> system

$\text{H}_2\text{S} + \text{MDEA} \rightleftharpoons \text{HS}^- + \text{MDEAH}^+$		Instantaneous	
$\text{CO}_2 + \text{H}_2\text{O} + \text{MDEA} \rightleftharpoons \text{HCO}_3^- + \text{MDEAH}^+$		$R_2 = k_2[\text{CO}_2][\text{MDEA}] - k_{-2}[\text{HCO}_3^-][\text{MDEAH}^+]$	
$K_{\text{H}_2\text{S}} = \frac{[\text{HS}^-][\text{MDEAH}^+]}{[\text{H}_2\text{S}][\text{MDEA}]}$	38.34	Dimensionless	Littel <i>et al.</i> (1990a), Blauwhoff <i>et al.</i> (1980)
$K_{\text{CO}_2} = \frac{[\text{HCO}_3^-][\text{MDEAH}^+]}{[\text{CO}_2][\text{MDEA}]}$	114.9	Dimensionless	Littel <i>et al.</i> (1990a), Blauwhoff <i>et al.</i> (1980)
$m_{\text{H}_2\text{S}}$	2.17	Dimensionless	Versteeg <i>et al.</i> (1988)
$m_{\text{CO}_2}$	0.72	Dimensionless	Versteeg <i>et al.</i> (1988)
$k_2$	$5.21 \times 10^{-3}$	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$	Littel <i>et al.</i> (1990b)
$D_{\text{CO}_2}$	$9.32 \times 10^{-10}$	$\text{m}^2 \text{s}^{-1}$	Versteeg <i>et al.</i> (1988)
$D_{\text{H}_2\text{S}}$	$9.27 \times 10^{-10}$	$\text{m}^2 \text{s}^{-1}$	Versteeg <i>et al.</i> (1988)
$D_{\text{MDEA}}$	$4.37 \times 10^{-10}$	$\text{m}^2 \text{s}^{-1}$	Versteeg <i>et al.</i> (1988)

Table 6. Process conditions for the simultaneous absorption of H<sub>2</sub>S and CO<sub>2</sub>

[MDEA] <sub>0</sub>	2000					mol m <sup>-3</sup>
<i>P</i>	10					bar
<i>T</i>	298					K
<i>k<sub>g</sub></i>	$1 \times 10^{-2}$					ms <sup>-1</sup>
<i>r<sub>1</sub></i>	50					μm
<i>s<sub>p</sub></i>	0.5					Dimensionless
<i>q</i>	3					Dimensionless
[CO <sub>2</sub> ] <sub>0</sub>	40					mol m <sup>-3</sup>
[HCO <sub>3</sub> <sup>-</sup> ] <sub>eq</sub>	1404					mol m <sup>-3</sup>
[H <sub>2</sub> S] <sub>0</sub>	0.01	0.1	1	10	mol m <sup>-3</sup>	
[HS <sup>-</sup> ] <sub>eq</sub>	40.3	124.8	368.1	938.6	mol m <sup>-3</sup>	

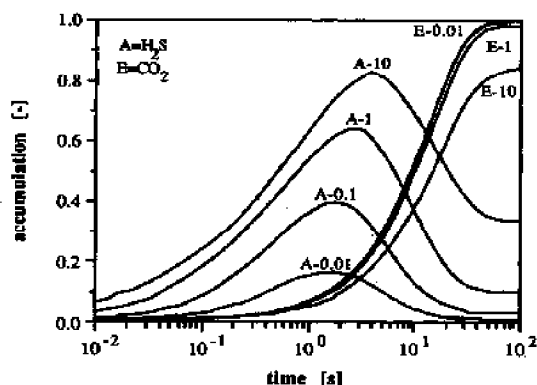


Fig. 17. Simultaneous absorption of H<sub>2</sub>S and CO<sub>2</sub> by a MDEA-impregnated particle. The conditions are mentioned in Tables 5 and 6. The gas concentration of H<sub>2</sub>S is varied and given in mol m<sup>-3</sup>.

50 μm offer interesting possibilities for the selective removal of H<sub>2</sub>S. In Table 5 typical data for the MDEA-H<sub>2</sub>S-CO<sub>2</sub> system are given. The products MDEAH<sup>+</sup>, HS<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> are ionic; therefore, total coupling of these species was assumed to maintain electroneutrality throughout the liquid. The diffusivity of the free amine ion MDEAH<sup>+</sup> will be, as a consequence of the highest molecular volume, lower than the diffusivities of HS<sup>-</sup> and HCO<sub>3</sub><sup>-</sup>, and almost equal to the diffusion coefficient of MDEA. In the

simulations the components MDEAH<sup>+</sup>, HS<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> were, therefore, given diffusion coefficients identical to the diffusivity of MDEA.

In Fig. 17 the results are shown for the process conditions given in Table 6. The gas-phase concentration of H<sub>2</sub>S is varied between ≈0.0025 and 2.5%, with, in all simulations, a concentration of ≈10% CO<sub>2</sub>. At low H<sub>2</sub>S concentrations the influence of the parallel reaction of CO<sub>2</sub> on the accumulation of H<sub>2</sub>S is very pronounced, and under these conditions the reversibility of the H<sub>2</sub>S reaction is of importance. At low H<sub>2</sub>S concentrations the absorbed H<sub>2</sub>S is, at high contact times, almost completely stripped from the liquid by means of the CO<sub>2</sub> coabsorption. Schrauwen (1985) treated both reactions (1c) and (2b) in a cyclone spray scrubber as independent and irreversible, but these examples indicate that even for very low liquid loadings this assumption is questionable. The examples also indicate that the residence time is a very important parameter to achieve an optimal usage of the amine for the separation of H<sub>2</sub>S.

In the present simulations a constant gas concentration of both H<sub>2</sub>S and CO<sub>2</sub> was assumed, while in gas treating processes the gas concentrations vary with the position in the absorber. Consequently, incorporation of the present micromodel in a reactor model will be necessary to study the gas absorption at changing gas concentrations. In future work such a reactor model will be presented for plug flow for the gas as well as the solid phase in a countercurrent and cocurrent mode of operation.

## 6. CONCLUSIONS

The absorption of gaseous components in porous particles impregnated with a reactive liquid phase has been studied theoretically. A model that describes this absorption process has been developed in which it is assumed that the porous particles act as a liquid support and are chemically inert. The model is based on the description of diffusion and reaction in a stagnant liquid sphere, and validated with several asymptotic analytical solutions.

Both reactions instantaneous with respect to mass transfer and reactions with finite reaction rates have been treated. For some asymptotic situations analytical solutions were derived. For instantaneous reactions an approximation for the dimensionless total accumulation is presented. This approximation gives accurate results if the diffusivities of the reactants and products are of the same order of magnitude and the physical accumulation of the gas is small compared to the product concentration. For reactions with finite reaction rate constants, different absorption regimes can be recognized in the time-flux diagrams.

If two gases are absorbed simultaneously in the liquid-impregnated particle, and both react with the same reactant, one gas component can, under specific conditions, selectively be absorbed. This offers interesting possibilities for the selective removal of  $H_2S$  from gases which also contain  $CO_2$  with aqueous amine solutions.

## NOTATION

$A_t$	total accumulation of A in the particle at time $t$ , mol
$A_\infty$	total accumulation of A in the particle at the end of the absorption process, mol
$[A], [E]$	concentration of absorbed component, $\text{mol m}^{-3}$
$[B], [C], [D], [F]$	concentration of non-volatile reactants and products, $\text{mol m}^{-3}$
$D$	diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
$D_m$	weighted diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
$E_a$	enhancement factor, dimensionless
$J_a$	flux of absorbed component A, $\text{mol m}^{-2} \text{s}^{-1}$
$k_{n,m}$	forward reaction rate constant for first reaction, $(\text{mol m}^{-3})^{(-n-m+1)} \text{s}^{-1}$
$k_{p,q}$	reverse reaction rate constant for first reaction, $(\text{mol m}^{-3})^{(-p-q+1)} \text{s}^{-1}$
$k_{r,s}$	forward reaction rate constant for second reaction, $(\text{mol m}^{-3})^{(-r-s+1)} \text{s}^{-1}$
$k_{u,v}$	reverse reaction rate constant for second reaction, $(\text{mol m}^{-3})^{(-u-v+1)} \text{s}^{-1}$
$k_g$	gas-phase mass transfer coefficient, $\text{m s}^{-1}$
$K_1$	equilibrium constant for first reaction, $(\text{mol m}^{-3})^{-n-m+p+q}$
$K_2$	equilibrium constant for second reaction, $(\text{mol m}^{-3})^{-r-s+u+v}$
$m_a$	partition coefficient of A, dimensionless
$p_{n1}$	expressed by relation (14b)
$p_{n2}$	expressed by relation (14c)

$[P]$	expressed by relation (18)
$q$	tortuosity, dimensionless
$r_1$	radius of sphere, m
$r$	radius, m
$R_1, R_2$	reaction rate for first and second reaction, $\text{mol m}^{-3} \text{s}^{-1}$
$t$	time, s
$w_n^2$	expressed by relation (14d)

## Greek letters

$\gamma_i$	stoichiometric coefficient in relations (1a) and (2a)
$\epsilon_p$	porosity, dimensionless
$\phi'$	Thiele modulus, expressed by relation (26b)
$\theta$	initial concentration

## Subscripts

eq	at equilibrium conditions
g	gas phase
0	initial concentration

## Superscripts

$n, m, p, q$	reaction orders in reaction rate expression $R_1$
$r, s, u, v$	reaction orders in reaction rate expression $R_2$

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